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LIQUID CHROMATOGRAPHY OF CARBAMATE PESTICIDES

Alfred D. Thruston, Jr.

Environmental Protection Agency
Athens, Georgia

October 1972

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Environmental Protection Technology Series

Liquid Chromatography of Carbamate Pesticides

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LIQUID CHROMATOGRAPHY OF CARBAMATE PESTICIDES,

Thruston, A. D., Jr.

Environmental Protection Agency, Athens, Georgia,
Southeast Environmental Research Laboratory

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Project No. 16020 EWC###

Environmental Protection Technology Series

Report No. EPA-R2-72-079, October 1972. 15 p, 3 fig, 3 tab, 6 ref.

Standard solutions of 23 carbamate pesticides prepared in isopropanol were analyzed using a DuPont Model 820 liquid chromatograph equipped with an ultraviolet photometric detector. Stainless steel columns (1 m x 2 mm i.d.) packed with either Permaphase ODS (octadecyl silane) or Permaphase ETH (ether) were used with the following mobile phases: 6 and 30 percent MeOH in water, hexane, one percent isopropanol/hexane, and 4 percent isopropanol/hexane. The retention times of the pesticides are given. The UV detector required 20-1500 ng for the pesticides studied to give a 25 percent full-scale recorder response. (Holoman-Battelle)

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*Liquid chromatography, *Retention time, Baygon, Furadan, Matacil, Mobam, Sevin, UC 10854, UC 8454, Carbanolate, RE 5305, Mesurol, Zectran, Ultraviolet detectors, Carbaryl, Aprocarb, Carbofuran, Aminocarb, Terbutol, Dazomet, Methonyl, Sirmate (2,3-isomer), Sirmate (3,4-isomer), Bux, Azak, Benomyl, IPC, CIPC, Dimetilan, Temik, Swep, Barban, Thiram, Mylone, Lannate

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EPA-R2-72-079
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LIQUID CHROMATOGRAPHY OF CARBAMATE PESTICIDES

by

Alfred D. Thruston, Jr.
Southeast Environmental Research Laboratory
College Station Road
Athens, Georgia 30601

Project 16020 EWC
Program Element 1B1027

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ABSTRACT

A commercial liquid chromatograph was evaluated and found useful for analysis of carbamate pesticides. Liquid chromatography retention times for 23 carbamate pesticides are given. The UV detector required 20 to 1500 ng for the pesticides studied to give a 25% full-scale recorder response.

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SECTION I

CONCLUSIONS

Liquid chromatography shows promise for analysis of carbamate pesticide residues. The technique provides separations with speed and resolution comparable to those of gas chromatography. Ambient or near ambient temperature can be used with heat-labile compounds. Sensitivity is 2 to 3 orders of magnitude less than that of electron capture gas chromatography but is still adequate for many compounds.

SECTION II

INTRODUCTION

Most carbamate pesticides cannot be analyzed directly by gas chromatography unless conversion to more suitable derivatives is carried out (1,2), because they are thermally unstable. Techniques, such as semi-quantitative thin-layer chromatography (3,4) or quantitative ultra-violet spectrometry (5), vary in selectivity and sensitivity.

Liquid chromatography (LC) is a relatively new analytical tool that offers selectivity and moderate sensitivity for analysis of these heat-labile compounds. LC separation and detection of Sevin (carbaryl) and its hydrolysis product, 1-naphthol, from plant extracts have been reported (6), but no comprehensive list of retention times and sensitivities of various carbamate pesticides has been published.

A liquid chromatograph is similar to a gas chromatograph; each has an injection port, a packed column, and a detector. A liquid mobile phase under pressure is used in LC instead of a carrier gas as in gas chromatography. Many compounds that are not volatile enough or too heat-labile for analysis by gas chromatography will partition between the LC stationary and mobile phases.

Two DuPont stationary phase columns were evaluated for analysis of carbamate pesticides--Permaphase ODS (for non-polar compounds) and Permaphase ETH (for more polar type carbamates).

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SECTION III

EXPERIMENTAL

Liquid chromatograph.--A DuPont Model 820 liquid chromatograph equipped with an ultraviolet photometric detector that measures the absorbance at 254 nm was used. The following columns and conditions were employed:

(1) 1m x 2mm id stainless steel column, packed with Permaphase ODS (octadecyl silane). Mobile phases were 6% and 30% methanol in water. A pressure of 1000 psi at 50° C maintained a flow of 1 ml/min.

(2) 1m x 2mm id stainless steel column, packed with Permaphase ETH (ether). Mobile phases were hexane, 1% isopropanol/hexane, and 4% isopropanol/hexane. A pressure of 400 psi at 40° C maintained a flow of 1 ml/min.

Solvents.--Spectrograde hexane, isopropanol, methanol and methylene chloride.

Standard carbamate solutions.--Standards (Table I) were prepared as isopropanol solutions.

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Table 1. Chemical names and sources of the carbamate pesticides

Common or Trade Name	Chemical Name	Source
Baygon^{R} (aprocarb)	2-isopropoxyphenyl-N-methyl carbamate	Chemagro Corp.
Furadan^{R} (carbofuran)	7-(2,3-dihydro-2,2-dimethyl)-benzofuranyl-N-methyl carbamate	Niagara Chem. Div., FMC Corp.
Matacil^{R} (aminocarb)	4-dimethylamino-3-methylphenyl-N-methyl carbamate	Chemagro Corp.
Mobam^{R}	4-benzothienyl-N-methyl carbamate	Mobil Chem. Co.
Sevin^{R} (carbaryl)	1-naphthyl-N-methyl carbamate	Union Carbide Corp.
Landrin	3,4,5-trimethylphenylmethyl-carbamate	Shell Development Corp.
UC 10854	3-isopropylphenyl-N-methyl carbamate	Union Carbide Corp.
UC 8454	1-(5,6,7,8-tetrahydro)-naphthyl-N-methyl carbamate	Union Carbide Corp.
Carbanolate	3,4-xylyl-6-chloro-N-methyl carbamate	Upjohn Co.
RE 5305	3-sec-butylphenyl-N-methyl carbamate	Chevron Chem. Co.
Mesurol^{R}	4-methylthio-3,5-dimethylphenyl-N-methyl carbamate	Chemagro Corp.
Zectran^{R}	4-dimethylamino-3,5-dimethyl-phenyl-N-methyl carbamate	Dow Chem. Co.

Table 1. Chemical names and sources of the carbamate pesticides

Common or Trade Name	Chemical Name	Source
Sirmate[R], 2,3-isomer	2,3-Dichlorobenzyl-N-methylcarbamate	FDA[a]
Sirmate, 3,4-isomer	3,4-Dichlorobenzyl-N-methylcarbamate	FDA[a]
Bux[R]	3-(1-Methylbutyl) phenyl methylcarbamate	Chevron Chem. Corp.
Azak[R] (terbutol)	2,6-Di-tert.-butyl-4-methylphenyl-N-methylcarbamate	Hercules Powder Co.
Benomyl (Dupont Fungicide 1991)	Methyl 1-(butylcarbamoyl)-2-benzimidazole carbamate	E. I. DuPont de Nemours and Co.
IPC	isopropyl-N-phenyl carbamate	PPG
CIPC	isopropyl-N-(3-chlorophenyl) carbamate	PPG
Dimetilan[R]	3-(1-N,N-dimethylcarbamoyl-5-methyl)-pyrazolyl-N,N-dimethyl carbamate	Geigy Chem. Corp.
Temik[R]	2-methyl-2-methylthio propion-aldehyde-0-methylcarbamoyl oxime	Union Carbide Corp.
Swep	methyl-N-(3,4-dichlorophenyl) carbamate	Niagara Chem. Div., FMC Corp.
Barban	4-chloro-2-butynyl-N-(3-chloro-phenyl) carbamate	Gulf Res. & Dev. Co.

Table 1. Chemical names and sources of the carbamate pesticides

Common or Trade Name	Chemical Name	Source
Thiram	bis(dimethylthiocarbamoyl) disulfide	E.I. Dupont de Nemours and Co.
Mylone^{R}(dazomet)	3,5-dimethyl-1,3,5-tetrahydrothiadiazine-2-thione	Union Carbide Corp.
Lannate^{R}(methomyl)	methyl N-[(methylcarbamoyl)oxy]-thioacetimidate	E.I. Dupont de Nemours and Co.

[a]Food and Drug Administration, Washington, D.C.

SECTION IV

RESULTS AND DISCUSSION

Table 2 lists retention times and sensitivities for 17 carbamates on Permaphase ODS. The first 12 eluted as sharp symmetrical peaks within 10 minutes with 6% methanol in water as the mobile phase; Figure 1 shows a chromatogram of five of these carbamate pesticides and 1-naphthol. The last five in Table 2 had excessive retention times, which were shortened by changing the mobile phase to 30% methanol in water.

Figure 2 shows chromatograms of seven of the more polar carbamates on the Permaphase ETH column. A change in mobile phase polarity from 1% isopropanol in hexane to 4% isopropanol in hexane causes significant changes in retention times. Table 3 summarizes retention times and minimum sensitivities of nine polar carbamates.

For these carbamates, the sensitivity of the UV detector ranges from 20-1500 ng, a level suitable for pesticide residue analysis. This work was done with pure solutions to obtain standard retention times. Natural sample extracts were not studied systematically.

The LC technique was applied to a study of the kinetics of Sevin degradation by micro-organisms. Aqueous samples of 4-8 µl were injected into the LC without prior clean-up or extraction. Sevin was observed in these samples in the 11-33 mg/ℓ range based on comparison with standard solutions.

Considerably lower detection limits can be obtained by concentrating the sample. For example, a liter of tap water, spiked with 2 µg/l of swep (methyl dichlorophenyl carbamate) was extracted with methylene chloride (3) and concentrated to 200 µl. Figure 3 shows a distinct swep peak in the chromatogram of a 5-µl injection of the concentrate.

Table 2. Retention times and sensitivities of various carbamates on Permaphase ODS column, 50° C, methanol/water mobile phase, 1000 psi, 1 ml/min flow rate, UV detector.

Chemical Name	6% MeOH/ H_2O R_t (min)	30% MeOH/ H_2O R_t (min)	Min. Amount to give 25% FSD (ng)
Baygon	1.50		250
Furadan	1.60		300
Matacil	2.00		50
Mobam	2.10		25
Sevin	2.60		100
Landrin	3.25		1000
UC 10854	3.40		1000
UC 8454	3.50		1000
Carbanolate	3.60		1000
1-naphthol[a]	4.30		250
RE-5305	7.20		1000
Mesurol	7.65		200
Zectran	8.30		200
Sirmate, 2,3-isomer		2.30	1500
Sirmate, 3,4-isomer		2.60	1500
Bux		3.50	1500
Benomyl[b]		6.10	1500
Azak		6.35	1500

[a] hydrolysis product of Sevin
[b] broad skewed peak

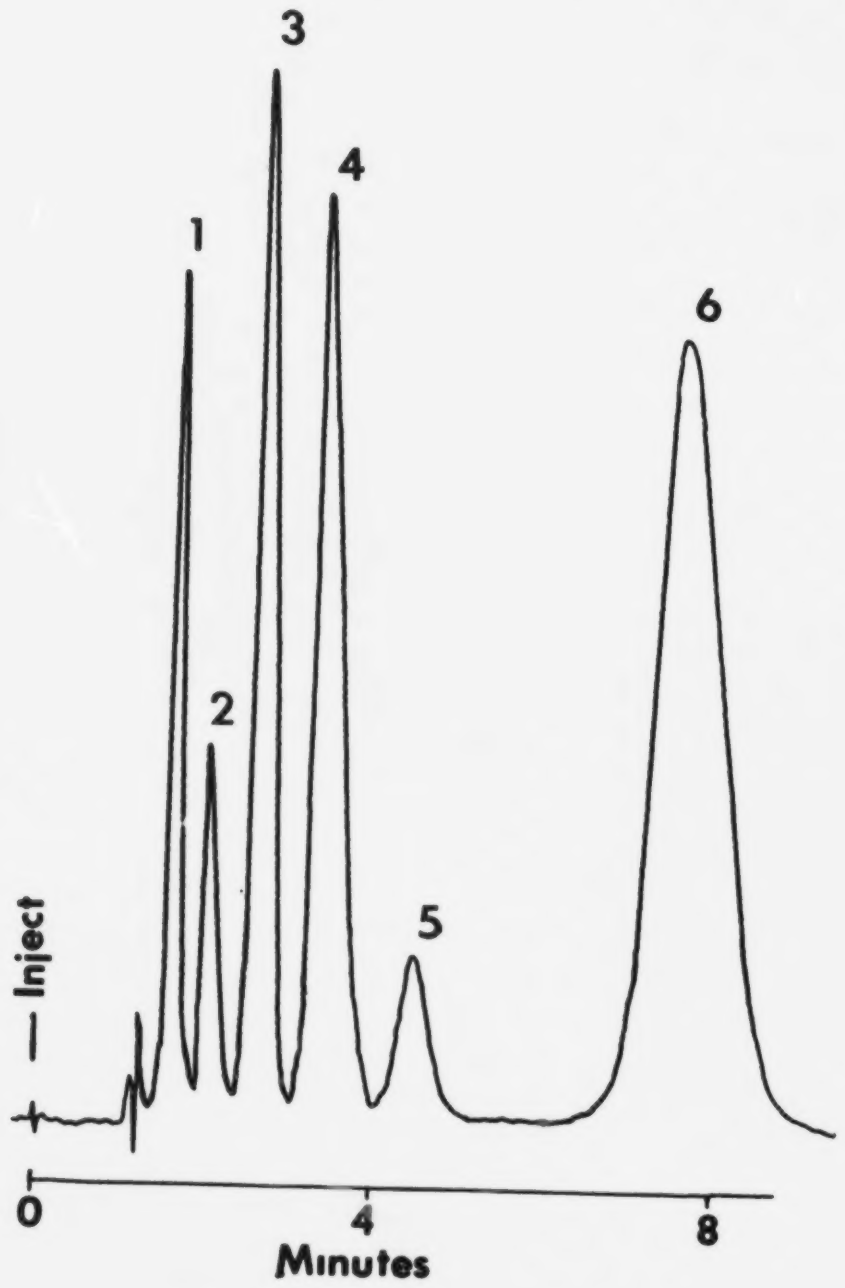

Figure 1. Chromatogram of carbamate pesticides on Perma-phase ODS column. 6% methanol/94% water mobile phase. 1, Furadan; 2, Matacil; 3, Sevin; 4, Landrin; 5, 1-naphthol (hydrolysis product of Sevin); 6, Mesurol.

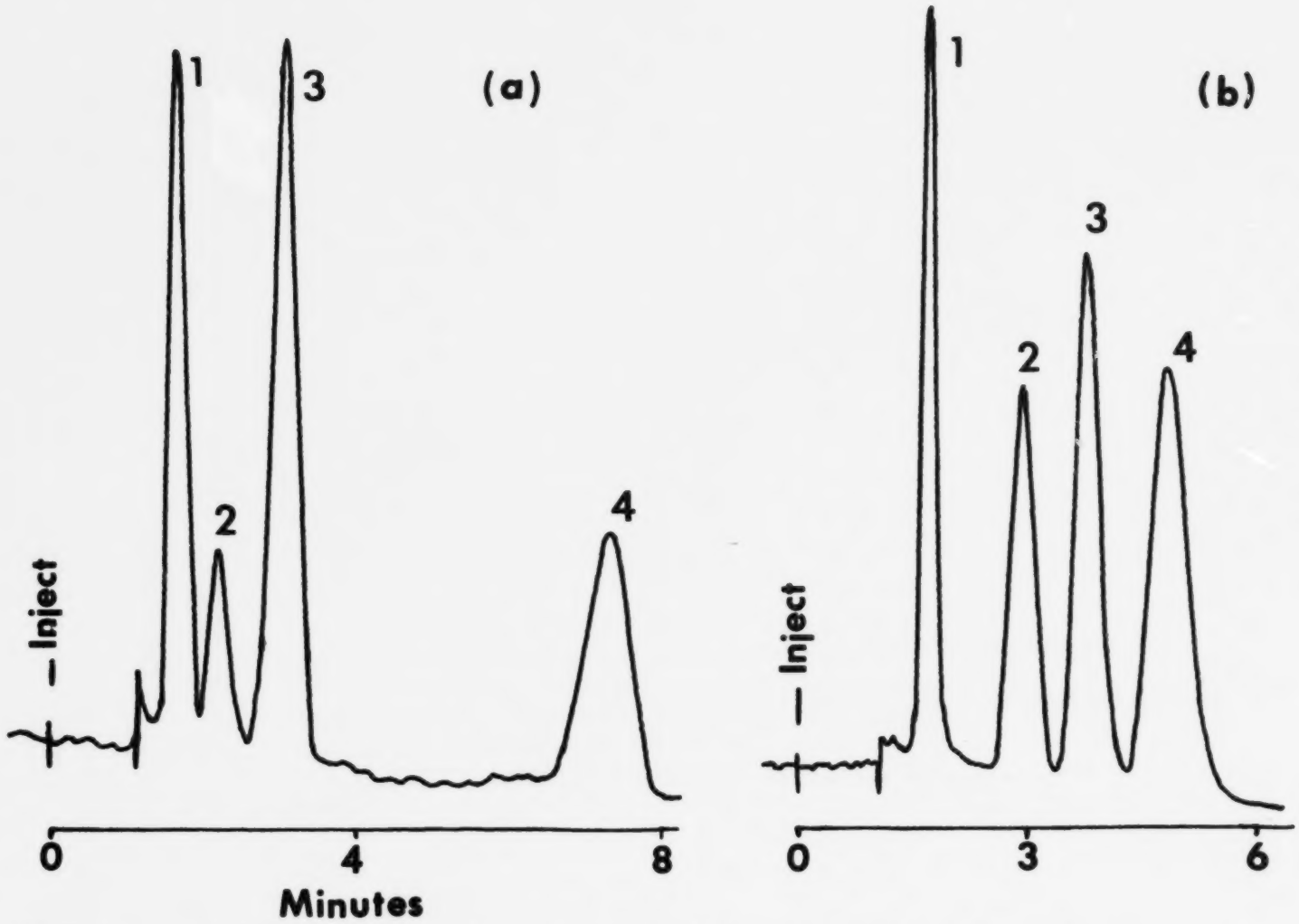

Figure 2. Chromatogram of carbamate pesticides on Permaphase ETH column: (a) 1% isopropanol/99% hexane mobile phase. 1, CIPC; 2, Dimetilan; 3, Temik; 4, barban. (b) 4% isopropanol/96% hexane mobile phase. 1, swep; 2, barban; 3, Mylone; 4, Lannate.

Table 3. Retention times and sensitivities of various carbamates on Permaphase ETH column, 40 °C, 0 to 4% isopropanol/hexane mobile phase, 400 psi, 1 ml/min flow rate, UV detector.

Chemical Name	Hexane R_t (min)	1% IPA/Hex R_t (min)	4% IPA/Hex R_t (min)	Min. Amount to give 25% FSD (ng)
IPC	1.52	1.50		250
CIPC	1.92	1.50		500
Dimetilan		2.10		1000
Temik		2.66	1.68	100
Swep		3.00	1.80	20
Barban		7.20	2.96	400
Thiram			2.90	50
Mylone			3.82	100
Lannate			4.88	500

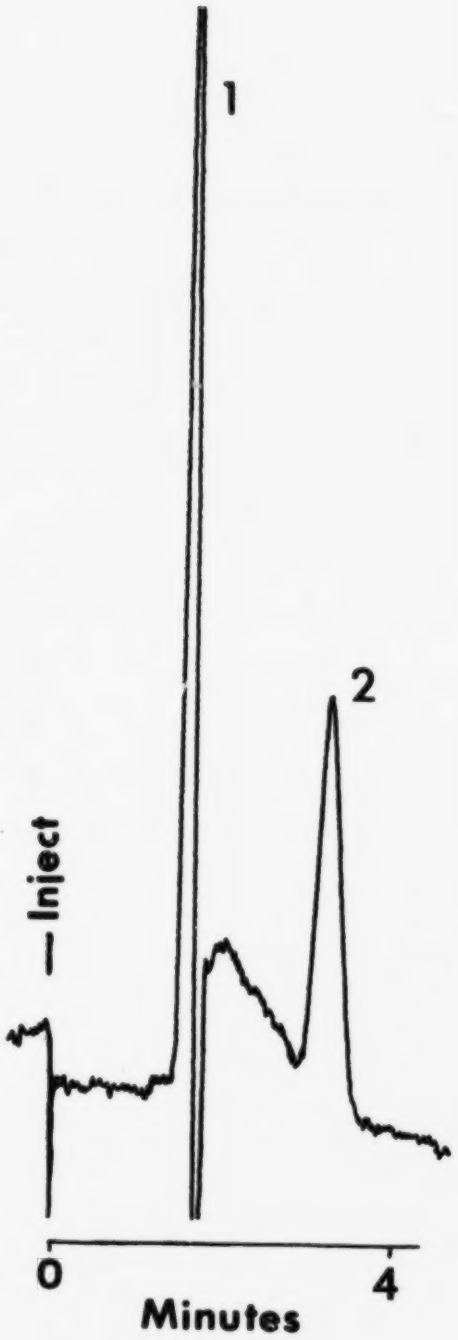

Figure 3. Chromatogram of swep, extracted from water spiked at 2 µg/ℓ level. 1, solvent peak; 2, swep.

SECTION V

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Thruston, A.D., Jr.

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Abstractor: A.D. Thruston, Jr.
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